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(54) Title: METHOD AND ARRANGEMENT FOR RECOVERING CHEMICALS FROM FLY ASH IN A GASIFICATION PROCESS

(57) Abstract: Method for recovering chemicals in conjunction with gasification of residual products from pulp production, the said gasification taking place under understoichiometric conditions, with formation of at least one phase of solid and/or molten material and at least one phase of combustible gaseous material. The principal gasification material supplied for gasification is a mixture of electric filter ash from a recovery boiler process and a support fuel in fluid form, which consists of one or more liquids from the group comprising sulphate soap, tall oil, turpentine or methanol, where the ratio between the electric filter ash and the support fuel is such that there are essentially equal quantities. By this means, it is possible to achieve a sufficiently high temperature to reduce the said sulphur-containing material. The invention means that a product liquid in the form of white liquor, which can be returned to the pulp process, can be obtained without intermediate causticization, while at the same time a considerable waste problem is solved and sodium and/or sulphur compounds are returned to the process. The invention also relates to an arrangement for mixing liquid support fuel with the electric filter ash.

Method and arrangement for recovering chemicals from fly ash in a gasification process.

TECHNICAL FIELD

The present invention relates to a method for recovering chemicals in conjunction with gasification of residual products from pulp production, the said gasification taking place under understoichiometric conditions, with formation of at least one phase of solid and/or molten material and at least one phase of combustible gaseous material, after which the said phases of solid and/or molten material are separated from the said phases of combustible gaseous material in order to be cooled and dissolved in a liquid and collected as a product liquid.

The invention also relates to an arrangement for supplying a mixture of materials, which are to be gasified, to a reactor for understoichiometric gasification, preferably of residual products which have been generated within the mill from a pulp production process, which gasification of the supplied mixture of materials takes place with formation of at least one phase of solid and/or molten material and at least one phase of combustible gaseous material.

PRIOR ART AND PROBLEMS

For very many years, the commercially dominant process for recovering chemicals from so-called black liquor, obtained when producing paper pulp in accordance with the kraft method, has conventionally been the so-called Tomlinson process which uses a so-called recovery boiler.

Swedish Patent SE-C-448,173 describes a more modern process which is based on understoichiometric

gasification/pyrolysis (i.e. with a deficit of oxygen) of the black liquor in a reactor. In this context, the products are a phase of solid and/or molten material, mainly comprising sodium carbonate, sodium hydroxide and sodium sulphide, and an energy-rich combustible gas phase, mainly comprising carbon monoxide, carbon dioxide, methane, hydrogen and hydrogen sulphide. The mixed solid/molten phase and gas phase are cooled and separated from each other in a separating part, which is connected to the reactor, by means of direct contact with green liquor, with the solid/molten phase being dissolved in the green liquor. The green liquor is then conveyed to conventional causticization for producing white liquor. The gas phase is used as fuel for generating steam and/or electric power.

WO91/08337, EP 617,747 and WO96/14468 are examples of further developments of the process which is described in SE-C-448,173. These patent applications deal with the problem of being able to directly produce a white liquor of high sulphidity in the black liquor gasification process, i.e. without the need for causticization, or with less need for causticization. The process is based on sulphur-containing material being recovered from the fuel gases from the gasification, or at least recovered from within the mill, and being supplied to the reactor. By means of the supply of sulphur-containing material, the reaction equilibrium is shifted towards increased production of sulphide, usually sodium sulphide and/or potassium sulphide. WO96/14468 also describes how, by means of several gasification reactors, the process can be tailored for production of liquors of different quality/sulphidity.

It is also known to integrate a gasification process with a recovery boiler process, which is described for example in WO93/11297. It is also known, from US Patent 5,562,804, to combust sulphate soap, in addition to

black liquor, in a recovery boiler, where the sulphate soap constitutes a source of sodium which binds sulphur in odour gases to form sodium sulphate, which is collected as so-called electric filter ash from the recovery boiler. At the same time, the energy content of the sulphate soap is used for producing steam.

Depending on the sodium/sulphur balance in the process among other things, the electric filter ash in the electric filter of the recovery boiler, sometimes as much as 40 - 50 tons per day, today often represents a residual product, which has to be disposed of. This involves both environmental and economic disadvantages and loss of chemicals which have to be replaced with make-up chemicals. Other sulphur-containing residual products are also generated in a pulp and paper mill and cause the same problems with regard to their handling.

DISCLOSURE OF THE INVENTION

The present invention makes available a method for recovering chemicals in conjunction with gasification of residual products from pulp production, which method reduces or eliminates the abovementioned problems. The fluids delivered for gasification consist essentially of fluids generated within the mill and the need for addition of make-up chemicals is thereby reduced.

The invention involves an improved method for direct production of white liquor of high sulphidity without the need of causticization. By means of the invention, the waste problems concerning the electric filter ash are solved, and at the same time it is possible to obtain a product liquid (white liquor) which can be recirculated and which is directly converted and can thus be used without an intermediate causticization process.

According to the invention, this is achieved by means of the method according to Patent Claim 1.

In a preferred embodiment, a mixture of electric filter ash and sodium-containing/sulphur-containing residual products from within the mill is gasified, it being possible for the gasification process to be driven with the reaction equilibrium shifted towards maximum sulphide production and thus increased sulphidity of the white liquor produced, preferably converted directly without any intermediate causticization process.

It has surprisingly been found that a support fuel, preferably consisting of one or more energy-rich fluids generated within the mill, preferably fluids rich in hydrocarbon and/or fluids of organic origin, whose exotermic reactions in the reactor gives the necessary energy development to reduce the present sulphur compounds, preferably the electric filter ash. According to the invention, the said support fuel consists of one or more liquids from the group comprising sulphate soap, tall oil (a refined form of sulphate soap obtained by cooking sulphate soap with phosphorous acid), and also turpentine and methanol. These support fuels which constitute residual products of pulp production are often extracted from black liquor (sulphate soap, tall oil) and condensate (turpentine, methanol) and accordingly there can be a limited amount of black liquor left, for sulphate soap typically 1 - 5%.

By supplying a mixture of electric filter ash and support fuel, a high temperature favouring the endothermic reactions in the reactor can be maintained within the reactor. The temperature is preferably at least 900°C, and still more preferably at least 1000°C. The pressure in the reactor can be atmospheric pressure

or about 1.5 - 15 bar (abs.), preferably 1.5 - 4 bar (abs.).

The increased energy development in the reactor also provides the conditions for converting sulphur-containing material to sulphide. By means of this conversion, with a shifted reaction equilibrium, the liquor produced in the gasification has a high sulphidity, which means that it can be used directly as a cooking liquor, white liquor, without causticization being required. The actual reaction equilibrium follows the reaction equation:

$$Na_2CO_3 + H_2S \Leftrightarrow Na_2S + H_2O + CO_2$$

According to one aspect of the invention, the said sulphur-containing material consists of one or more materials generated within the mill, of which at least some are in a fixed phase, such as electric filter ash from a recovery boiler process, which electric filter ash is preferably transferred from the recovery boiler process while essentially maintaining the same high temperature. Other sulphur-containing substances generated within the mill and which can conceivably be added to the gasification are methyl mercaptan, dimethyl sulphide, dimethyl disulphide, hydrogen sulphide, residual acid (sulphuric acid containing sodium sulphate) from production of chlorine dioxide, sulphur-containing solutions from soda pan scrubbers, etc.

According to a further aspect of the invention, solid sulphur-containing material is dispersed in the support fuel before being supplied to the reactor.

The invention also relates to an arrangement for mixing sulphur-containing material and support fuel for onward transport to a reactor.

DESCRIPTION OF THE FIGURES

The invention will now be described with reference to the figures, of which:

Fig. 1 shows a recovery system for a preferred embodiment of the method according to the invention,

Fig. 2 shows an arrangement for mixing sulphur-containing material and support fuel for onward transport to a reactor, and

Fig. 3 shows an alternative recovery system according to the invention in its simplest form.

In Fig. 1, reference number 1 designates a gasification reactor for production of a white liquor 2 of high sulphidity, preferably a sulphidity of at least 50%. The reactor 1 operates at a pressure of 1.5 bar (abs.) and at a temperature of about 950°C. The reactor 1 is integrated with a conventional recovery boiler 3 in a system for recovering chemicals from residual products of chemical pulp production from raw fibre material.

In a preferred embodiment of the invention, in addition to the mixture of electric filter ash and sulphate soap, another support fuel, also admixed therewith, and chosen from the group comprising methanol, tall oil or turpentine, is delivered to the gasification reactor, this being the application shown in Figure 1.

Black liquor 4 from the pulp production consists, in the preferred embodiment, of the thin liquor from the pulp digester or evaporated black liquor, and is fed to the recovery boiler 3. The black liquor stream 4A to the recovery boiler 3 is evaporated 5 to the required conventional dry content and is heat-treated 6 for expelling any gaseous sulphur compounds 7, for example methyl mercaptan, dimethyl sulphide, dimethyl

disulphide and hydrogen sulphide, which are fed to the gasification reactor 1 in order to contribute to shifting the reaction equilibrium therein towards an increased amount of sulphide in the produced liquor 2.

The recovery boiler 3 produces a green liquor 8 of relatively low sulphidity, which green liquor is causticized to white liquor of low sulphidity in a conventional manner. Electric filter ash 9, is separated as a residual product from the electric filter of the recovery boiler and, preferably while retaining its high temperature, is transferred in amounts of about 40 - 50 tons per day to the gasification reactor 1 in accordance with the invention, in order to be converted there to sulphide. Further gaseous sulphur compounds 11, principally hydrogen sulphide, are recovered 10 from the fuel gas 12 from the gasification reactor and expediently returned to the gasification reactor. The remainder of the fuel gases 13 is expediently fed to a conventional gas boiler or incinerator furnace for steam generation(not shown).

The electric filter ash 9 is expediently mixed with support fuel (in the form of sulphate soap/tall oil or other energy-rich fluid 14 generated in the mill) in a first mixer m1 before delivery to the reactor 1. Other residual products 14B, different from those mixed in the first mixer, alternatively a second amount of residual products, are admixed in a downstream mixer m2. As an example sulphate soap/tall oil can be admixed in the first mixer and methanol/turpentine in the second mixer. When mixed, the sulphate soap ought to be at a high temperature to obtain a proper viscosity level.

The addition of a support fuel in the gasification process, ensures that the necessary high temperature can be maintained in the reactor 1 for

converting/reducing the electric filter ash 9 to sulphide form.

To enable energy development in the reactor 1, oxygen-containing gas 15/15a is supplied, for example compressed air, oxygen gas or a destruction gas with a substantial excess of oxygen. However, the amount of oxygen gas supplied is only so much that the gasification process remains understoichiometric with respect to oxygen. The sulphate soap 14 moreover acts as a tenside for the mixture, which results in optimum drop formation during gasification.

In the simplest application of the invention, the reactor is supplied only with electric filter ash 9 and support fuel 14, which in Figure 1 means that the subsidiary stream 14B and the mixer m2 are omitted. Figure 3 shows such a system in which only the electric filter ash 9 and sulphate soap 14 are fed to the reactor 1 after previous mixing in the mixer m. The functions which are similar to those shown in Figure 1 have been given the same reference labels. In Figure 3, a gas boiler GB is also used, to which hydrogen sulphide H_2S and air 15b are fed, and from which sulphur dioxide is obtained which can be used in other processes such as bisulphite, sulphite or CTMP processes.

In gasification trials without substantial presence of black liquor, and where essentially equal proportions of support fuel, in the form of sulphate soap, and of electric filter ash were fed to the reactor, a fuel gas was obtained with a heat value (LHV) of 2345 kJ/Nm^3. The product liquid which was obtained from the melt had a very high sulphidity level of the order of 67% Na_2S, 8% NaOH and 25% Na_2CO_3. In certain applications, such a product liquid can be returned to the pulp production process without intermediate causticization.

In a second gasification trial without substantial presence of black liquor, and where the ratio of sulphate soap to electric filter ash was 4:5, a fuel gas was obtained with a heat value (LHV) of 2049 kJ/Nm^3. The product liquid which was obtained from the melt had an even higher sulphidity level of the order of 70% Na_2S, 7% NaOH and 23% Na_2CO_3.

In the trials mentioned above, there was no recirculation of H_2S recovered from the fuel gases, which recirculation can considerably increase the sulphidity level of the product liquid.

Fig. 2 shows an arrangement for mixing a support fuel into a sulphur-containing material in solid phase. The solid sulphur-containing material preferably consists of electric filter ash in particulate form which is preferably transferred in the warm state from the electric filter of the recovery boiler to a container 20 with an outlet sluice 21 at the bottom. The electric filter ash is dosed and fed via the outlet sluice 21 into the lower part of a first transport device 22a consisting of a transport screw 24a which slopes upwards in the transport direction and is driven by a motor 29a. In the lower part of the transport screw 22a is opening a line 23 for sulphate soap at preferably lower temperature, or other support fuel, which sulphate soap is sucked into the warm electric filter ash and thus impregnates this ash. The electric filter ash and the sulphate soap are mixed in the transport screw and are transported upwards and forwards towards a first overflow outlet 28a where the mixture is transferred to the lower part of a second transport device 22b which is preferably of the same type as the first transport device 22a, with a transport screw 24b driven by a motor 29b. Also opening into the lower part of the second transport device 22b is a line 25 for the other residual products and/or a second stage with sulphate soap. By means of the second transport screw

24b, a renewed mixing and transportation is obtained upwards and forwards towards a second overflow outlet 28b, where the mixture flows over to a pump box 26 and a pump 27, preferably with impeller wheels, for onward transport to the gasification reactor.

In a simplier embodiment in which only electric filter ash and sulphate soap are to be supplied to a reactor, the second impregnation stage may be omitted, i.e. the first transport device then feeds directly to the pump box 26.

Since the electric filter ash normally contains chlorides which ought to be bleeded out of the system some kind of chloride separation process can be installed. The chloride separation process can be installed in different positions in the process, for example as a chrystallization cooling process or warm leaching process of the electric filter ash, modification of the gasification process or as a subsequent treatment of the obtained white liquor.

The invention is not limited to the described embodiments and instead can be varied within the scope of the attached patent claims. It will be appreciated, for example, that the method can also be carried out with other transport devices for sulphur-containing material and support fuel, either as mixtures or individually. It will further be appreciated that naturally occurring potassium compounds can be used in addition to sodium compounds. The residual products generated within the mill can also be supplemented with or replaced by corresponding residual products which have been generated outside the mill, for example from another pulp production mill.

PATENT CLAIMS

1. Method for recovering chemicals in conjunction with gasification of residual products from pulp production, the said gasification taking place under understoichiometric conditions, with formation of at least one phase of solid and/or molten material and at least one phase of combustible gaseous material, after which the said phases of solid and/or molten material are separated from the said phases of combustible gaseous material and then cooled in order to dissolve the said phases of solid and/or molten material in a liquid which is collected as a product liquid (2), c h a r a c t e r i z e d i n that the principal material supplied for understoichiometric combustion is a mixture of: - electric filter ash (9) from a recovery boiler process, and

- a support fuel (14) which consists of one or more liquids from the group comprising sulphate soap, tall oil, turpentine and methanol, and in that the ratio between the said electric filter ash and the support fuel is such that there are essentially equal quantities, by which means a temperature can be maintained during gasification which is sufficient to reduce the said sulphur-containing material to sulphide.

2. Method according to Claim 1, c h a r a c t e r i z e d i n that the gasification takes place at a temperature in the range of 700 - 1400°C, preferably 900 - 1200°C.

3. Method according to Claim 2, c h a r a c t e r i z e d i n that the said electric filter ash is transferred from the recover boiler process while retaining essentially the same high temperature.

4. Method according to Claim 3, c h a r a c t e r i z e d i n that the ratio between the said sulphur-containing material and the support fuel is such that there is a preponderance of sulphur-containing material of the order of 10 - 20%.

5. Method according to any of the preceding claims, c h a r a c t e r i z e d i n that gaseous sulphur compounds, principally hydrogen sulphide, are recovered from the fuel gas obtained from the understoichiometric gasification in the reactor, and in that this recovered sulphur compound is returned to the gasification reactor.

6. Method according to any of the preceding claims, c h a r a c t e r i z e d i n that the stoichiometry during the gasification is maintained at a level which is normal for understoichiometric gasification, preferably with addition of an oxygen-containing gas (15) in an amount which corresponds to 40 - 60%, preferably 45 - 50%, of the amount of oxygen which would be needed in stoichiometric terms to ensure complete combustion of the compounds which are formed on gasification.

7. Arrangement for supplying a mixture of materials, which are to be gasified, to a reactor for understoichiometric gasification of residual products generated within the mill from a pulp production process, which gasification of supplied material takes place with formation of at least one phase of solid and/or molten material and at least one phase of combustible gaseous material, c h a r a c t e r i z e d i n that the arrangement comprises:

- a container (20) for electric filter ash (9),
- a first transport device (22a) which is operatively connected, preferably mechanically connected, to the container and which is intended to

transport the said electric filter ash (9) in the direction towards the said reactor, and

- a supply device (LC) for supplying at least one support fuel (23), which support fuel consists of one or more liquids from the group comprising sulphate soap, tall oil, turpentine and methanol, connected to the first transport device near the container (20) so that the support fuel can thus be mixed/impregnated with the sulphur-containing material during transport in the transport device in the direction towards the said reactor.

8. Arrangement according to Claim 7, c h a r a c t e r i z e d i n that the arrangement comprises:

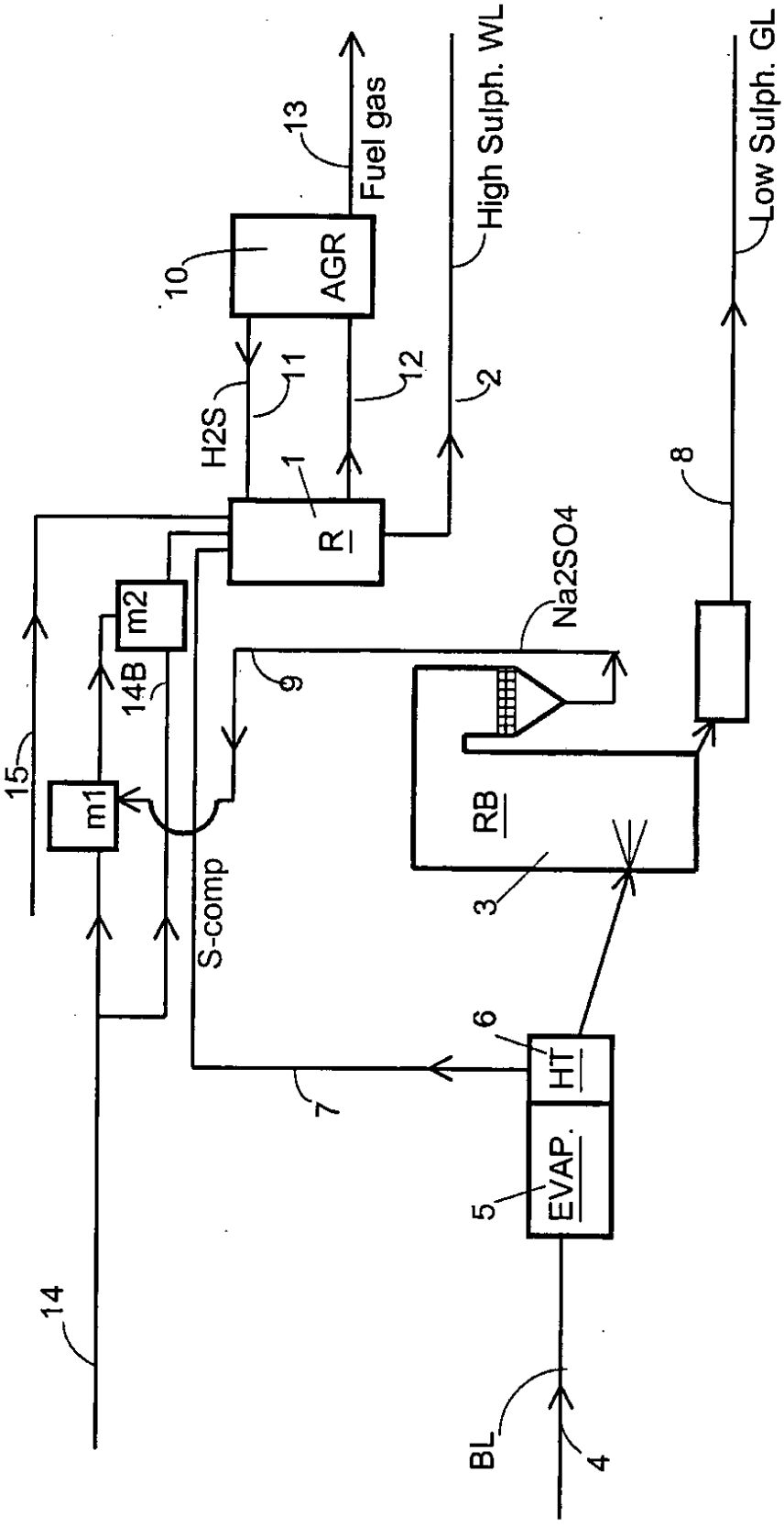
- a second transport device (22b), preferably mechanical, is connected to the first transport device (22a) and which is intended to transport the said sulphur-containing material (9), mixed/impregnated with the support fuel, in the direction towards the said reactor,

- a supply device (LC) for a second support fuel (25), which support fuel consists of one or more liquids from the group comprising sulphate soap, tall oil, turpentine and methanol, connected to the second transport device near its connection to the first transport device (22a), so that the sulphur-containing material mixed/impregnated with support fuel can thus also be mixed/impregnated with additional support fuel in a second stage during transport in the direction towards the said reactor.

9. Arrangement according to Claim 8, c h a r a c t e r i z e d i n that the said first and second transport devices (22a, 22b) each consist of a transport screw (24a, 24b) sloping essentially upwards in the transport direction, with an overflow outlet (28a, 28b) for the transported material, and with one

or more inlets, located in the bottom part thereof, for the transported material.

10. Arrangement according to any of Claims 7 to 9, c h a r a c t e r i z e d i n that a collecting vessel (26) is arranged to receive the mixed/impregnated material downstream of the second transport device, and a pump (27) is arranged to agitate and transfer the transported material from the collecting vessel to the said reactor.


Fuel gas
High Sulph. WL
Low Sulph. GL
13
10
AGR
11
12
2
H2S
1
R
8
Na2SO4
m2
14B
9
15
m1
RB
3
S-comp
6
HT
7
EVAP.
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BL
4

FIG. 1

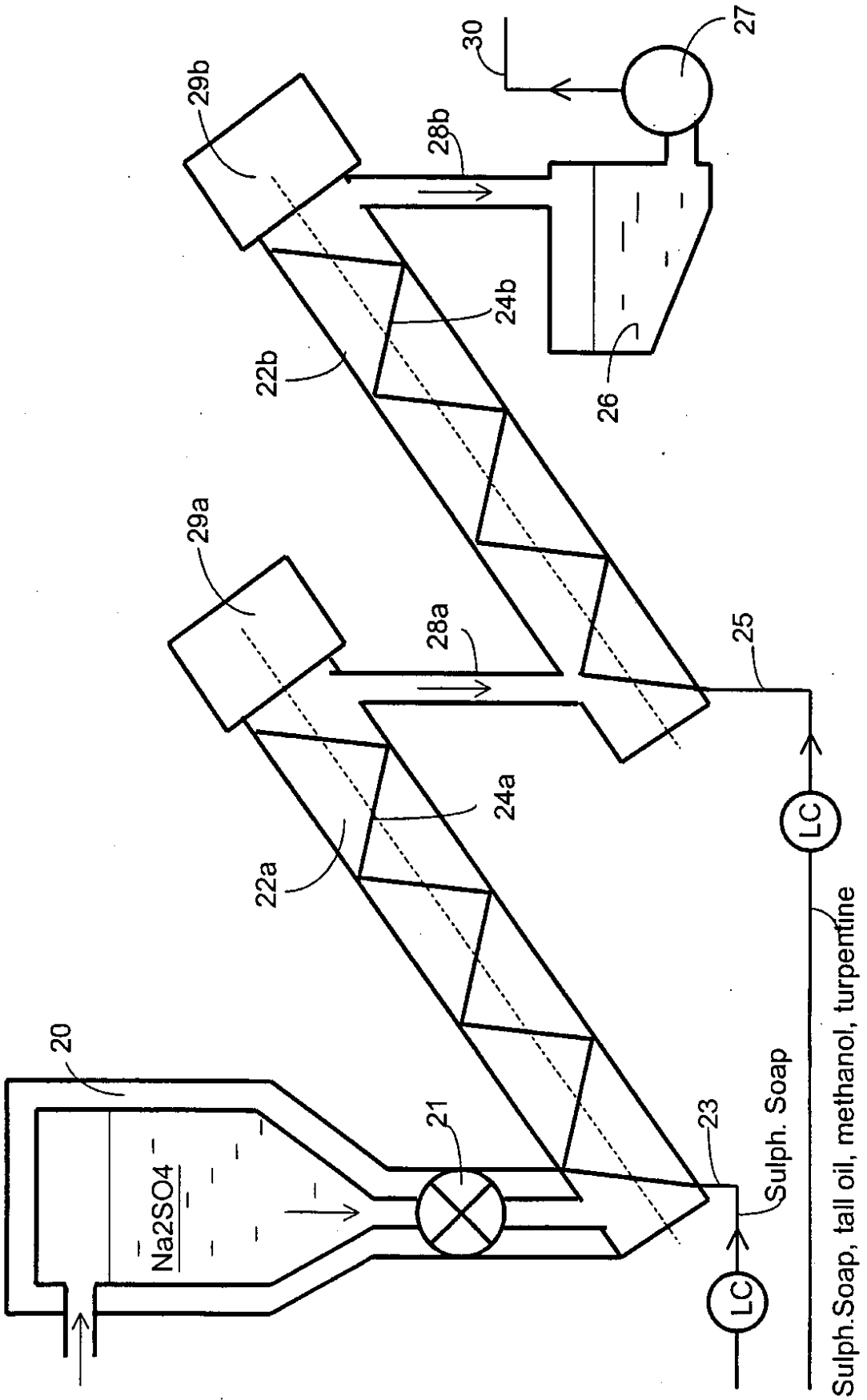

FIG. 2

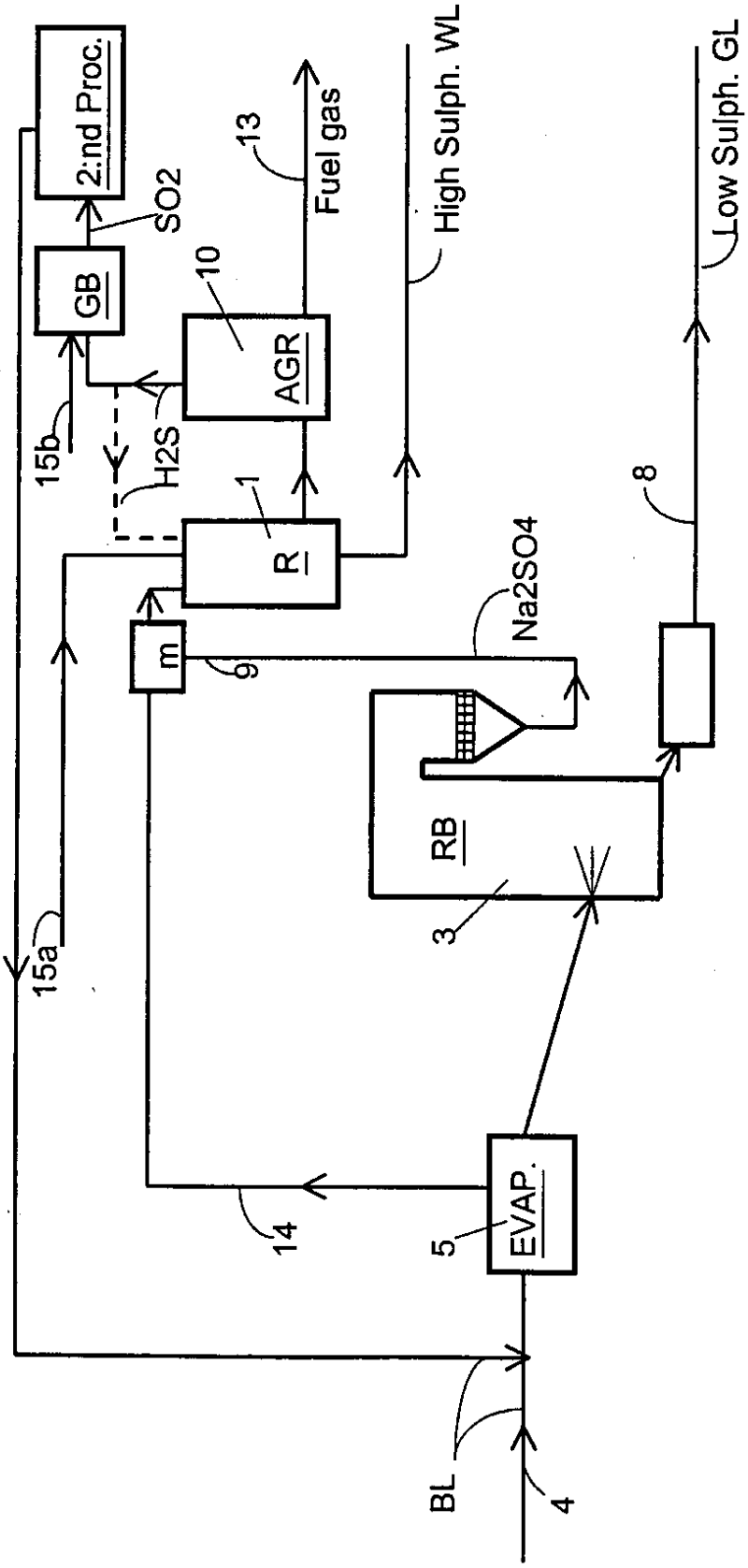

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 00/01979

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21C 11/12, D21C 11/04
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5328563 A (KAJ HENRICSON ET AL), 12 July 1994 (12.07.94), abstract --	1-10
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 February 2001	21 -02- 2001
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Marianne Bratsberg/ELY Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

05/02/01

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